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(21) International Application Number: PCT/US90/05037 (22) International Filing Date: 6 September 1990 (06.09.90) (30) Priority data: 404,240 7 September 1989 (07.09.89) US (71) Applicant: HEXCEL CORPORATION [US/US]; 11555 Dublin Boulevard, Dublin, CA 94568 (US). (72) Inventors: MYERS, Warren, D. ; 235 Pickering Place, Wal- nut Creek, CA 94598 (US). BISHOP, Ernest, M. ; 1780 Jennifer Drive, Livermore, CA 94550 (US). (74) Agent: HEINES, M., Henry; Townsend and Townsend, One Market Plaza, 2000 Steuart Tower, San Francisco, CA 94105 (US).		(81) Designated States: AT (European patent), AU, BE (Euro- pean patent), CH (European patent), DE (European pa- tent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (Euro- pean patent), JP, KR, LU (European patent), NL (Euro- pean patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: THERMOPLASTIC HONEYCOMB AND METHODS OF PREPARATION (57) Abstract Thermoplastic honeycomb capable of formation by expansion of a compacted ribbon stack and of repeated dips in resin solution to form densified honeycomb panels is prepared by impregnating a fiber web with a thermoplastic material which has a soluble form and an insoluble form, and is readily converted from the former to the latter. Poly(amide-imide)s are an example of a suitable resin. The invention is particularly useful in forming compacted ribbon stacks of resin-impregnated glass fiber, expanding the stacks at an elevated temperature to a partial expansion sufficient to expose the cell interiors, then dipping the partially expanded stacks in resin solution, removing the solvent from the resulting film and curing the film, then expanding the stacks further at an elevated temperature to their full expansion, following by further dips to the final desired density.		

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THERMOPLASTIC HONEYCOMB AND METHODS OF PREPARATION

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This invention lies in the fields of honeycomb structures and polymer processing techniques. The particular area addressed by this invention is that relating to honeycomb structures formed of fabric-reinforced polymer.

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BACKGROUND AND SUMMARY OF THE INVENTION

Honeycomb has long been known for use in structural elements where a combination of lightness and strength are desirable. The use of nonmetallic materials such as ceramics and plastics offers additional advantages in terms of processing characteristics and the appearance and properties of the final product.

Thermoset plastics have been used in the manufacture of honeycomb, by fusing together corrugated ribbons of the plastic as well as by fusing together ribbons of fabric impregnated with thermosetting resin prior to the final cure. Difficulties with such materials include limitations on the manufacturing techniques, as well as minimal damage resistance with the result that the product is highly susceptible to damage during fabrication and lay-up, as well as fragmentation upon handling.

The present invention provides honeycomb based on plastic materials, the honeycomb being of acceptable mechanical properties and capable of being fabricated and handled by simpler and more versatile techniques. As described herein, honeycomb structures can be prepared which have the strength, impact resistance and processing characteristics of thermoplastic materials and yet offer high temperature resistance and solvent resistance characteristics which permit such processing steps as the application of multiple coatings for purposes of density adjustment and the formation of composite layers.

Central to the invention is the selection of a thermoplastic resin which has a soluble form and can be converted to an insoluble form. A fiber web is initially impregnated with the resin in its soluble form, using any of a variety of techniques, thereby fusing the fibers together into a stable coherent structure. The resulting impregnated web, in the form of ribbons or sheets, is arranged in a stack, in which adjacent ribbons or sheets are fused together along transverse node lines to render the stack expandable into the open-cell structure which forms the honeycomb, the expansion facilitated by heating the stack up to the softening point of the resin. The thermoplastic character of the insoluble resin permits this expansion to occur without damage to the resin, and the character of being insoluble permits further applications of the resin subsequent to the initial expansion. The soluble form of the resin permits these applications to be made by dipping the expanded structure in a solution of the resin followed by removal of the solvent and conversion to the insoluble form. Expansion can be done in stages, with further applications of resin in between each stage. The technique can also be used to apply layers of different resins or coating materials to form for example a composite structure with a specified combination of properties. In preferred embodiments, the initial impregnation is also done by dipping the fiber web in a solution of the resin in its soluble form.

Other advantages, features and embodiments of the invention will be apparent from the description which follows.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The present invention has wide applicability in terms of the types of honeycomb which can be formed and the various procedural steps and different types and numbers of layers to be applied as well as the means by which they are applied. The invention is of particular interest however as applied to thermoplastic-impregnated fabric in unexpanded stacks of ribbons or sheets which are then expanded into open-cell honeycomb panels to which further thermoplastic resin is

applied by dipping the expanded honeycomb into a solution of the resin. In accordance with this application, a wide variety of resins can be used, subject to the description in the preceding section. The choice of resin can thus depend on the
5 choice of solvents.

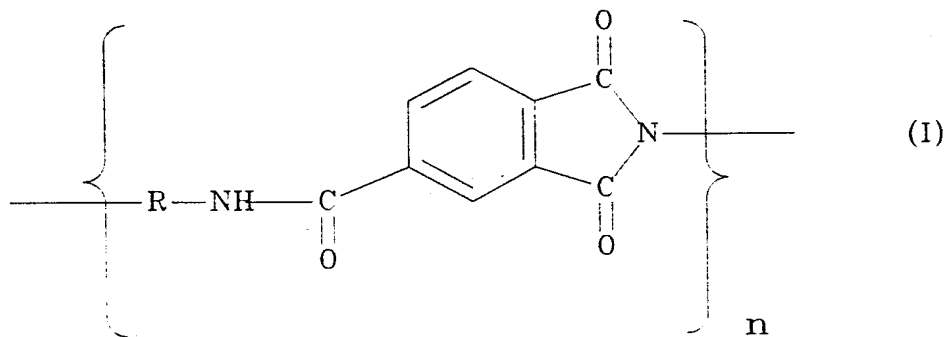
The resin serving as the fabric impregnant may be the same as or different than the resin in the dip solution, and where more than one dip solution is used, the resins in the solutions themselves may be the same or different. When
10 different resins are combined in either of these two ways in a single honeycomb structure, the resins must be compatible with each other. Compatibility in this context denotes the tendency of two resins to fuse together as one cures over a cured layer of the other, to the extent that the two are not easily
15 separated by physical or mechanical means. The combining of two or more resins in this fashion permits the formation of hybrid structures and the achievement of useful as well as synergistic properties.

The resin serving as the fabric impregnant may be one
20 which is applied in the same manner as the subsequent resin layers, i.e., by dipping followed by solvent removal and thermal conversion to a state permitting further processing. Alternatively, the fabric impregnant may be applied by other techniques known to those skilled in the art. Examples of
25 other techniques are electrostatic deposition of the resin directly onto the fiber web in dry powder form followed by thermal fusion, and hot calendering of the resin in solid form directly onto the fabric.

The resins used in the practice of the present
30 invention are thermoplastic resins which are soluble in a given solvent but which are capable of thermal conversion to a form which is insoluble in the same solvent. The term "thermal conversion" and related terms are used herein to denote a chemical reaction, such as curing or chain lengthening, which
35 occurs at elevated temperature. Any thermoplastic resin which meets this description may be used.

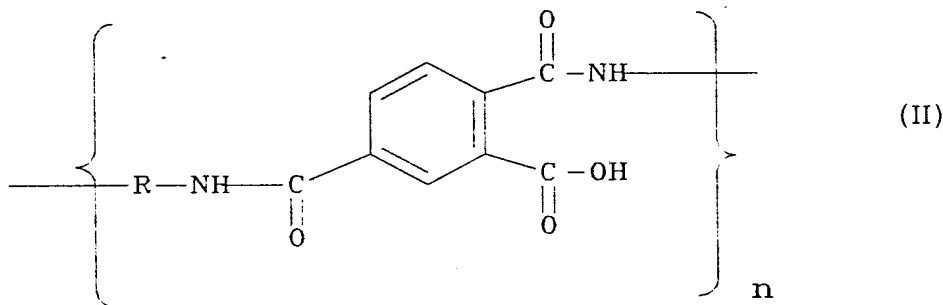
A wide variety of thermoplastic polymers may be used as the resins. Examples include polyamides, poly(amide-

imide)s, polyacetals, polycarbonates, poly(butylene terephthalate)s, poly(phenylene oxide)s and poly(phenylene sulfoxide)s. Preferred polymers for both the initial fabric impregnant and the dipping solution(s) are poly(amide-imides), particularly those of the following formula

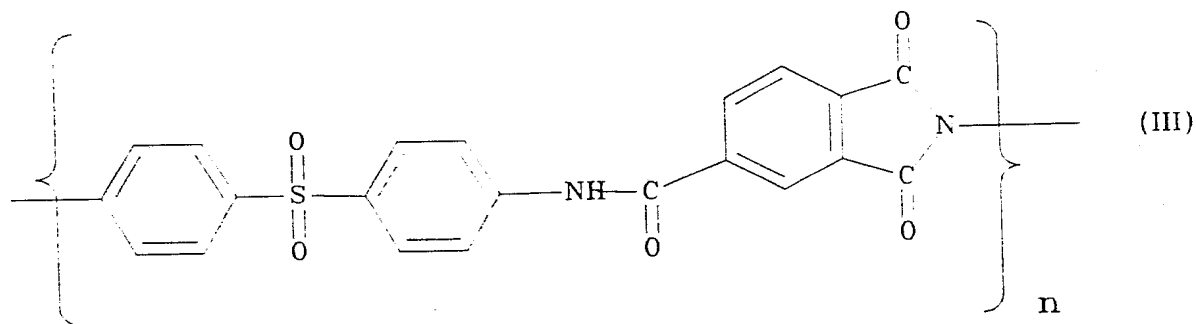


in which R is alkyl, preferably $\text{C}_1\text{-C}_6$, straight-chain or branched-chain; aryl, preferably phenyl, naphthyl, diphenyl sulfide, diphenyl sulfoxide or diphenyl sulfone; or aryl-alkyl combinations such as benzyl and diphenylmethylenes.

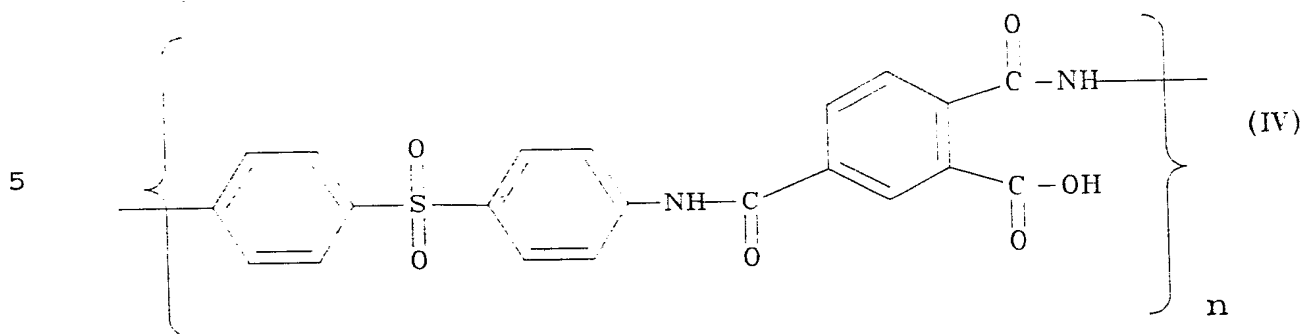
The formula shown above represents the polymer in reacted form, insoluble in any of a variety of polar organic solvents. The prepolymer is any precursor form of the above which is soluble in the same solvents. The precursor may be a partially polymerized analogue of the insoluble polymer, particularly one with a sufficient number of free acid groups remaining which render it soluble. One possibility for the precursor is a poly(amic acid) represented by the formula



A particularly preferred polymer within the scope of formula I above is one represented by the formula



for which the corresponding soluble poly(amic acid) prepolymer is as follows:



This poly(amic acid) is formed by the reaction between diamino diphenyl sulfone and trimellitic anhydride. Preferred poly(amic acids) within this formula as well as precursors in general to the polymer of formula II above are those having an acid number ranging from about 50 to about 100 when dissolved in a solvent as a 25% solution by weight. A prepolymer which has been found to be particularly effective is a product defined as AI-10 Polymer, supplied by Amoco Chemicals Corporation, Chicago, Illinois, which undergoes conversion at temperatures of 350°F and above.

The choice of solvent is not critical and may vary widely, provided that it dissolves the resin prior to its conversion to the insoluble state. Polar organic solvents are preferred, and examples are dimethylformamide, dimethylacetamide, dimethyl sulfoxide, N-methylpyrrolidone and *m*-cresol. The properties of the solution may be modified by the use of a diluent, which may be any liquid which is miscible with the solvent, does not cause premature precipitation of the unconverted resin, and yet does not dissolve the converted

polymer. Examples of diluents compatible with the solvents listed above are aromatic hydrocarbons, ethyl acetate, acetone, cyclohexanone, acetamide and acetanilide. The diluent may serve as an aid in removing the solvent, as for example by
5 evaporation, or as an additive for adjusting the viscosity of the solution, or both.

The concentration of resin in the solution may also vary, and will be chosen in accordance with the desired viscosity of the solution and other processing characteristics.
10 In most applications, best results will be obtained using solutions having a dissolved solids content (i.e., the resin) of about 10% to about 30% by weight, preferably from about 15% to about 25% by weight. One solution which has been found to be effective is a solution of the AI-10 polymer in a mixture of
15 40% acetone and 60% N-methylpyrrolidone, with a solids content of about 18% to 22% by weight.

The web or reinforcement may be any material capable of impregnation by a resin. Both woven and nonwoven fabrics may be used, including both natural and synthetic materials.
20 Reinforcements made from glass fibers are particularly useful. The porosity and weight of the fabric may also vary widely. In most cases, fabrics having a weight ranging from about 0.3 to about 3.0 ounces per square yard (10 to 100 grams per square meter), preferably from about 0.5 to about 2.0 ounces per
25 square yard (17 to 68 grams per square meter) will provide the best results.

Fabrication of the honeycomb may be done in accordance with known procedures. The term "honeycomb" is used herein to denote any open-cell grid structure, and particularly
30 such open-cell structures which are formed from fused sheet stacks which are expanded or drawn apart. Examples of such stacks and the honeycomb panels which they form upon expansion are found in Steele, R.C., et al., U.S. Patent No. 2,674,295 (April 6, 1954); Holland, K.M., U.S. Patent No. 3,006,798
35 (October 31, 1961); Anderson, D.C., et al., U.S. Patent No. 3,466,957 (September 16, 1969); Noble, R.G., et al., U.S. Patent No. 3,598,676 (August 10, 1971); and Taylor, R.S., U.S.

Patent No. 3,819,439 (June 25, 1974). The disclosures of these patents are incorporated herein by reference.

The fused stacks which are expanded into open-cell honeycomb structures may be of various dimensions of thickness, length and width. As addressed by the present invention, these stacks may be formed from components which range from long, narrow strips or ribbons, to relatively wide sheets. In practice, ribbon stacks are generally formed from sheet stacks by cutting with a band saw or similar equipment. Other methods of preparation are possible, however, and the present invention is not contemplated to be limited to any particular method or any particular configuration of the stack itself. For purposes of convenience, ribbons and sheets will be referred to herein generically as "layers."

As one example of a fabrication procedure, a roll of glass fiber fabric, typically 2 to 4 mils in thickness, is impregnated with a solution of the resin in its soluble state. An example, as stated above, is the AI-10 polymer dissolved in a 40/60 mixture of acetone and N-methylpyrrolidone at a solids content of about 20% by weight. The impregnated roll is then passed through an oven at a temperature of about 400°F (204°C) for 5 to 8 minutes, which results in the acetone and N-methylpyrrolidone being flashed off and the remaining resin being partially cured to a tack-free state. The roll is then cut into sheets. In one embodiment the roll is cut into sheets about 36 inches (91 cm) in width, on a 45° bias, i.e., in a direction such that the fibers are aligned at an angle of approximately 45° with respect to the lateral edges of the sheets. The longitudinal edges of the sheets are then overlapped, glued together and heat sealed. This is followed by rolling the sheets into rolls and heat soaking the rolls at about 350°F (177°C) for at least one hour for final curing of the glue.

Once the rolls are cured, they are unrolled and node lines, typically of a nylon-modified epoxy, are printed on them at regular intervals using a standard gravure technique. The rolls are then cut into rectangular sheets which are stacked to a thickness of about 4 to 5 inches (10 to 13 cm). The stacks

are then placed in a press where they are heated to a temperature of about 350°F (177°C) under a pressure of about 500 to 600 psi (35 to 42 kg/cm²) to cure the node adhesive, thus bonding the sheets together at the node lines. The result
5 is a stack ready for expansion into a honeycomb structure.

Since the cured resin is a thermoplastic material, the unexpanded honeycomb block may be expanded to the desired dimensions, and restrained in the expanded state by a jig or frame. For blocks made from webs with low resin content,
10 expansion may occur at room temperature. In most applications, however, particularly those involving anything other than very low resin loadings, expansion is best done with the aid of heat, such as by the use of steam and/or hot water. Thus expanded, the honeycomb may be dipped in fresh AI-10 solution
15 to form a film over the cured surface of the honeycomb. The solvent is then removed from the film and the resin converted to the final cured state in the same manner as the web impregnant. The dipping procedure may be repeated as often as desired to achieve a final honeycomb of the desired density and
20 other characteristics.

In particularly preferred embodiments, the initial expansion is done to less than a full expansion, opening the cells only part way to their maximum opening. This prevents excessive strain on the node bonds. The first dip followed by
25 solvent removal and cure is then performed while the cells are still only partially opened. The panel is then heated once again and expanded to its full expansion, opening the cells to their maximum opening, the node bonds being strengthened by the coating laid down by the dip. The expansion ratio prior to the
30 dip is not critical, and may range from about 20% to about 80% depending on the materials, conditions and dimensions of the system, although in most cases, an initial expansion ratio (i.e., the percent of total expansion) of about 50% will provide the best results.

35 The dipping process may be repeated several times, the number depending on the cell size and the desired final density. The most typical cells are hexagonal in shape, with a width of about one-quarter inch (0.6 cm) or less.

The foregoing is offered primarily for purposes of illustration. It will be readily apparent to those skilled in the art that modifications and variations may be made in the materials, proportions, conditions and procedures used without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A laminated structure expandable into an open-cell grid structure, comprising layers of fabric fused together at node lines periodically spaced along each said layer, said layers impregnated with a thermoplastic material which is insoluble in a selected solvent and capable of formation from a precursor by thermal conversion, said precursor being one which is soluble in said solvent.

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2. A laminated structure in accordance with claim 1 in which said selected solvent is a member selected from the group consisting of dimethylformamide, dimethylacetamide, dimethyl sulfoxide, N-methylpyrrolidone and *m*-cresol.

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3. A laminated structure in accordance with claim 1 in which said thermoplastic material is a poly(amide-imide).

4. A laminated structure in accordance with claim 1 in which said thermoplastic material is a poly(amide-imide) formed by the reaction between a diamino diphenyl sulfone and trimellitic anhydride.

5. A laminated structure in accordance with claim 1 in which said thermoplastic material is a poly(amide-imide) and said precursor is a prepolymer thereof having an acid number ranging from about 50 to about 100.

6. A laminated structure in accordance with claim 1 in which said fabric is a glass fiber web.

7. A method for preparing a fiber-reinforced thermoplastic laminate expandable into open-cell grid structure, said method comprising:

(a) impregnating a fiber web with a thermoplastic polymer which is insoluble in a selected solvent and capable of formation from a

prepolymer by thermal conversion, said prepolymer being one which is soluble in said solvent; and

5 (b) fusing together a plurality of layers of said fiber web so impregnated, at node lines periodically spaced along each said layer, to form a laminated structure.

8. A method in accordance with claim 7 in which said thermoplastic polymer is a poly(amide-imide) formed by the
10 reaction between a diamino diphenyl sulfone and trimellitic anhydride.

9. A method for preparing an open-cell grid structure comprised of a fiber-reinforced thermoplastic
15 laminate, said method comprising:

(a) impregnating a fiber web with a first thermoplastic polymer which is insoluble in a selected solvent;

20 (b) fusing together a plurality of layers of said fiber web so impregnated, at node lines periodically spaced along each said layer, to form a laminated structure;

25 (c) heating said laminated structure to a temperature at which said first thermoplastic polymer softens sufficiently to permit expansion of said laminated structure into an open-cell grid structure, and expanding said laminated structure so heated;

30 (d) immersing said expanded laminate so heated and expanded into a solution of a polymer precursor in said selected solvent, said polymer precursor being thermally convertible to a second thermoplastic polymer which is compatible with said first thermoplastic polymer and insoluble in said selected solvent to coat said open-cell grid structure with a
35 film of said solution; and

(e) removing said solvent from said film and thermally converting said polymer precursor to form a

coating of said second thermoplastic polymer over said layers.

10. A method in accordance with claim 9 in which the expansion of step (c) is a partial expansion resulting in an open-cell grid structure whose cells are partially opened, and said solution, polymer precursor and film are defined as a first solution, a first polymer precursor and a first film, respectively, and said method further comprises:

(f) heating said open-cell grid structure subsequent to step (d) to a temperature at which said first and second thermoplastic polymers soften sufficiently to permit further expansion of said open-cell grid structure, and further expanding said open-cell grid structure so heated;

(g) immersing said open-cell grid structure thus further expanded in a second solution of a second polymer precursor in said selected solvent, said second polymer precursor being thermally convertible to a third thermoplastic polymer which is compatible with said second thermoplastic polymer and insoluble in said selected solvent to coat said open-cell grid structure with a second film of said second solution; and

(h) removing said solvent from said second film and thermally converting said polymer precursor to form a coating of said third thermoplastic polymer over said coating of said second thermoplastic polymer.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/05037

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC <div style="text-align: center; font-family: monospace;"> INT.CL. (5): B32B 17/10 U.S. CL. 428/116, 285, 435 </div>											
II. FIELDS SEARCHED <div style="text-align: center; font-size: small;">Minimum Documentation Searched ⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="text-align: center; padding: 10px;">U.S.</td> <td style="text-align: center; padding: 10px;">428/116, 117, 285, 435</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	428/116, 117, 285, 435					
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; padding: 5px;">Category [*]</th> <th style="width: 70%; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 10px;">Y</td> <td style="padding: 10px;">US, A, 3,899,626 (STEFFEN) 12 AUGUST 1975 See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 10px;">1-10</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 10px;">Y</td> <td style="padding: 10px;">US, A, 4,710,432 (NISHIMURA) 01 DECEMBER 1987; See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 10px;">1-10</td> </tr> </table>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	US, A, 3,899,626 (STEFFEN) 12 AUGUST 1975 See the entire document.	1-10	Y	US, A, 4,710,432 (NISHIMURA) 01 DECEMBER 1987; See the entire document.	1-10
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>											
IV. CERTIFICATION <table style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-family: monospace; font-size: 1.2em;">20 NOVEMBER 1990</div> </td> <td style="width: 50%; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-family: monospace; font-size: 1.5em;">31 JAN 1991</div> </td> </tr> <tr> <td style="vertical-align: top;"> International Searching Authority <div style="text-align: center; font-family: monospace;">ISA/US</div> </td> <td style="vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;"> W.J. VanBalen </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-family: monospace; font-size: 1.2em;">20 NOVEMBER 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-family: monospace; font-size: 1.5em;">31 JAN 1991</div>	International Searching Authority <div style="text-align: center; font-family: monospace;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;"> W.J. VanBalen </div>					
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